The Reactions between Bis(styrene)bis(triphenylphosphine)-ruthenium(0) and Cyclohexene; its Relevance to the Alkene Isomerisation Reaction and to the Catalytic Disproportionation of Cyclohexene

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The reaction between bis(styrene)bis(triphenylphosphine)ruthenium(0) and cyclohexene produces the 1-5- η -cyclohexadienylhydridobis(triphenylphosphine)ruthenium(II) complex, $\text{RuH}(1-5-\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2\cdot\text{C}_6\text{H}_{10}$, whose structure has been determined by X-ray diffraction, and also two isomers of $\text{RuH}(1-3-\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2\cdot\text{C}_6\text{H}_{10}$.

$\text{RuH}(1-5-\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2$ can be prepared by the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ and cyclohexa-1,3-diene. In solution these complexes exist as a mixture of the 1-5- η and 1-3- η complexes and cyclohexene and detailed ^1H and ^{31}P nuclear magnetic resonance studies have been made. The complex $\text{RuH}(1-3-\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10})$ undergoes a reversible insertion of alkene into the $\text{Ru}-\text{H}$ bond. The relevance of this observation to the mechanism of alkene isomerisation is discussed. The catalytic disproportionation of cyclohexene to benzene and cyclohexane in solution has also been studied.

The reversible insertion of alkenes into metal hydrogen bonds is a key step in the isomerisation of alkenes using transition metal complex hydridic catalysts in homogeneous solution. The only system in which this reaction has been demonstrated¹ to occur on the NMR time scale, is the reversible insertion of ethylene into the $\text{M}-\text{H}$ bond of $\text{MoH}(\text{C}_2\text{H}_4)_2(\text{diphos})_2^+$, formed by protonation of $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$. Stable hydrido alkene complexes in which insertion is slow on the

NMR time scale are also known.² No systems in which alkene coordination to a complex metal hydride is followed by such a reversible insertion have been studied although this prior coordination is usually assumed. Hence no spectroscopic information is available for determining the relative rates of alkene coordination and insertion and for ascertaining which of these steps is rate determining in the isomerisation of alkenes using hydride metal catalysts in solution.

We have studied^{2,3} the reactions of various alkenes with hydrido ruthenium(II) and ruthenium(0) triphenylphosphine species and have shown that these reactions involve alkene coordination and insertion reactions although in some cases dehydrogenation of the alkene occurs, *e.g.*, of but-1-ene to give a buta-1,3-diene complex.

We now describe the reaction between the styrene complex, $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$, and cyclohexene. This reaction gives several products and ^1H and ^{31}P NMR studies on these provide some insight into the mechanism of the isomerisation of alkenes using hydridic ruthenium(II) complex catalysts.

RESULTS AND DISCUSSION

The reaction of the ruthenium(0) complex $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ with cyclohexene gives a series

Scheme 1. Proposed mechanism for the formation of cyclohexadienylhydrido complexes from the interaction of cyclohexene and $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$; $\text{P} = \text{PPh}_3$. Arrows indicate hydride shifts. Conformations of rings are not shown.

Scheme 2. The reaction of cyclohexene with $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$. (i) cyclohexene, (ii) argon sweep of toluene solution, (iii) recrystallise or stand in Nujol mull, (iv) cyclohexa-1,3-diene, (v) add PPh_3 and warm.

of products all of which have to be formulated as hydridobis(triphenylphosphine)ruthenium(II) species. These hydrido species are formed by reactions involving hydride transfer from cyclohexene to ruthenium as shown in Schemes 1 and 2.

The most stable compound, which can be isolated as yellow crystals, has the stoichiometry $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_{10}$ (**A**). It has to be formulated as a 1-5- η -cyclohexadienyl species that contains uncoordinated cyclohexene in the crystal lattice. The structure of this compound, determined⁴ by X-ray crystallography, confirms that the cyclohexene molecule is not coordinated and that the complex has the structure shown in Fig. 1.

An absorption at 2015 cm^{-1} in the infrared spectrum of **A** is assigned to $\nu_{\text{Ru-H}}$, whilst peaks at 2790 and 2760 cm^{-1} arise from $\nu_{\text{C-H}}(\text{exo})$ of the methylene group of the coordinated 1-5- η -cyclohexadienyl moiety⁵ and from uncoordinated cyclohexene (*cf.* 2703 cm^{-1} for free cyclohexene⁶).

On carrying out the reaction between $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ and cyclohexene under slightly different conditions (see Experimental), two other compounds, **B** and **C**, also of formula $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10})$ may be isolated. Recrystallisation of **B** or **C*** gives **A**.

* **C** is also converted quantitatively to **A** if a Nujol mull is allowed to stand for some hours.

Fig. 1. The structure of 1-5- η -cyclohexadienyl-hydridobis(triphenylphosphine)ruthenium(II),cyclohexene (1/1) as determined by X-ray diffraction. The cyclohexene is not coordinated to the metal and is omitted.

Evaporating a solution of **A**, **B** or **C** in toluene to dryness with an inert gas (to remove cyclohexene) produces another complex, $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ (**D**). The latter is more easily prepared by interaction of $\text{RuH}_2(\text{PPh}_3)_4$ with cyclohexa-1,3-diene and is a 1-5- η -cyclohexadienyl compound identical with **A** except that no cyclohexene is present.

The compounds **B**, **C** and **D** all show absorptions in the IR spectrum attributable to $\nu_{\text{Ru-H}}$ and to $\nu_{\text{C-H}}(\text{exo})$ of the methylene group of a coordinated cyclohexadienyl ligand, together with other peaks attributable to triphenylphosphine (see Experimental).

From the methods of preparation of the various compounds it appears that the transformations shown in Schemes 1 and 2 occur.

Other 1-5- η -cyclohexadienyl complexes of ruthenium are well-known and may be formed by nucleophilic attack of hydride on coordinated π -benzene complexes such as $[(\text{C}_6\text{H}_6)_2\text{Ru}]^{2+}$ ⁷ and $[\text{C}_6\text{H}_6\text{RuL}_3]^+$ ⁸.

¹H and ³¹P NMR spectroscopy. The ¹H NMR spectrum of the compound **D**, $\text{RuH}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2$, in toluene at 25 °C consists of a series of poorly resolved resonances at δ 4.9(1), 4.8(2), 2.6(3), 1.6(1) (relative intensities in parentheses) which can be assigned to protons 3; 2 and 2'; 1, 1' and 4; and

4' (Scheme 2), the *exo* proton of the methylene group resonating to high field of the *endo* proton.

The hydride resonance is a sharp triplet at δ -12.4 ($J_{\text{PH}}=27$ Hz). This is entirely consistent with the structure shown in Fig. 1.

The complex is isoelectronic and essentially isostructural with $(1\text{-}5\text{-}\eta\text{-C}_5\text{H}_5)\text{RuH}(\text{PPh}_3)_2$ ⁹ and $(1\text{-}5\text{-}\eta\text{-PhO})\text{RuH}(\text{PPh}_3)_2$ ¹⁰.

The noise decoupled ³¹P NMR spectrum consists of a single resonance at δ 61.5 ppm,* which splits into a doublet ($J_{\text{PH}}=27$ Hz) when coupling to the hydride is introduced, and a doublet of doublets ($J_{\text{PH}}=27$ and 8 Hz) when the phenyl region is selectively decoupled. This last observation suggests that the phosphorus atoms are coupled to one proton of the cyclohexadienyl moiety and we tentatively suggest that this is the *endo* proton. On cooling, the single ³¹P resonance broadens and splits (coalescence temperature ≈ 253 K) so that at -70 °C an **AB** quartet ($\delta_{\text{A}}=63.9$, $\delta_{\text{B}}=59.7$, $J_{\text{AB}}=17$ Hz) is observed. The two phosphorus atoms are thus non-equivalent and we suggest that this is caused by the adoption by the cyclohexadienyl ring of a conformation which destroys the two-fold axis of the rest of the molecule, as is found in the solid state when cyclohexene is present in the lattice⁴ (Fig. 1). Once again, the resonances split further into doublets ($J_{\text{PH}}=27$ Hz) when coupling to the hydride is introduced.

The ¹H NMR spectra of **A**, **B** and **C** at room temperature in benzene or toluene** are all identical and consist of resonances from $\text{RuH}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2$ (**D**) and from free cyclohexene together with a broad resonance at δ -5.6 and a sharper resonance at 2.65 ppm. This same spectrum is obtained if cyclohexene is added to $\text{RuH}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2$ (**D**) but the resonances mentioned above grow only slowly; similarly, freshly prepared solutions of $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_3 \cdot \text{C}_6\text{H}_{10}$ (**A**) do not show the resonances at δ 2.65 and -5.6 ppm but these grow slowly with time.

This suggests that these two resonances are from either **B** or **C** and since **C** is apparently thermodynamically more stable than **B** they probably arise from **C**.

On cooling cyclohexene solutions of **A**, **B** or **C**,

* All ³¹P chemical shifts are to high frequency of external 85 % H_3PO_4 .

** In CD_2Cl_2 an identical spectrum is obtained but, on standing, the resonances disappear and are replaced by resonances attributable to CD_2HCl , $\text{RuHCl}(\text{PPh}_3)_3$,¹¹ $(\pi\text{-C}_6\text{H}_6)\text{RuH}(\text{PPh}_3)_2^+ \text{Cl}^-$,¹⁰ benzene and cyclohexene.

the resonance at $\delta -5.6$ broadens until at *ca.* -20°C it is no longer visible. Further cooling causes little observable change until at -60°C a broad peak is observed at $\delta -17.6$. This sharpens considerably when the solution is irradiated in the position of the phosphorus resonance for this compound, but viscosity broadening and crystallisation problems have meant that we have been unable to achieve the low temperature limiting spectrum. Similar effects are observed in C_7D_8 but the resonance at $\delta -17.6$ is much weaker presumably because in the absence of excess cyclohexene the equilibrium (a) in Scheme 2 lies further to the left.

On account of the presence of excess cyclohexene it is difficult to detect what other resonances the resonance at $\delta -5.6$ gives rise to on cooling. However, new broad resonances are observed at δ 4.3, 2.8 and 2.2 ppm. These could arise from olefinic, *endo* and *exo* protons of the cyclohexene groups respectively. The sharp resonance at δ 2.65 disappears. It is clear that the resonance at $\delta -5.6$ ppm which is present at room temperature and which sharpens to a triplet ($J_{\text{PH}} \approx 6$ Hz) on warming to 60°C arises from dynamic exchange between a hydrido ligand ($\delta -17.6$ at -70°C) and some aliphatic protons.

The actual number of aliphatic protons taking part in the exchange reaction is difficult to assess, but since J_{PH} for hydrido protons in this kind of complex is typically^{3,10} *ca.* 30 Hz, and since the average J_{PH} in the fast exchange situation is 6 Hz, it seems likely that the total number of protons taking part in the exchange is five (one hydridic and four aliphatic).

From this evidence it seems probable that **B** and **C** contain a coordinated cyclohexene moiety and that the cyclohexadienyl group is only 1-3- η -, *i.e.*, it is bound by only three carbon atoms in a η_3 -allylic system, and has in addition an uncoordinated double bond. The free double bond in these complexes should show $\nu_{\text{C}=\text{C}}$ near 1655 cm^{-1} ^{12,13} but it is apparently too weak to be observed in our complexes; this kind of vibration is often weak.¹³

Even at -80°C we do not observe resonances from the 1-3- η -cyclohexadienyl ring but this is probably caused by ring gliding as in Equilibrium (d), Scheme 2, which we assume to be a low energy process. This would make the ring appear as a 1-5- η -ring on the NMR time scale and cause the resonances to lie underneath those from $\text{RuH}(\text{1-5-}\eta\text{-C}_6\text{H}_7)(\text{PPh}_3)_2$ (**D**). A similar effect has been reported for the 1-3- η - C_5H_5 ring of $(\text{C}_5\text{H}_5)_2\text{W}(\text{CO})_2$.^{14,15}

The temperature dependence of the ^1H NMR spectrum of **C**, the thermodynamically most stable product and hence, presumably, the one present in solution, is then best explained in terms of a reversible insertion of the cyclohexene group into the $\text{M}-\text{H}$ bond (Equilibrium (c) in Scheme 2). If the insertion and elimination reactions both occur with the same stereochemistry, then the hydride will exchange with four protons on the cyclohexene ring.

Thus, if the inversion and elimination reactions are stereospecifically *cis*, the metal will effectively move around on one side of the ring and exchange with the four methylene protons on one side of the ring. If no inversion of the ring occurs the metal would alternate between axial and equatorial positions. However, since the metal is a bulky substituent it presumably would prefer to be in an equatorial position and the ring would probably invert at each 1,2-shift, thus rendering equivalent the two olefinic protons and the four methylene protons which are not exchanging with the hydride ligand. This then accounts for the sharp singlet at δ 2.6 observed in the room temperature ^1H NMR spectrum. (The mean position expected for this resonance based on the individual chemical shifts is δ 3.1).

If, on the other hand, the insertion and elimination reactions are stereospecifically *trans*, the metal would move around the equatorial positions of the ring and the remaining six protons would be rendered equivalent despite the fact that no ring inversion would occur. (The mean position expected for the non-exchanging proton in this case would be *ca.* δ 2.9). It would appear that in either case the position of the resonance due to the protons exchanging with the hydride should be *ca.* $\delta -2$ rather than -5.6 and we are unable to explain this anomaly unless the chemical shift of one or more of the protons is itself temperature dependent.

Scheme 3. Alternative pathway for exchange of metal hydride with aliphatic protons in $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ (**C**).

Fig. 2. Possible structures of (1-3- η -cyclohexadienyl)-hydridoruthenium(II) species.

On the basis of the ^1H NMR evidence we cannot unequivocally rule out the possibility that the hydride is exchanging with some protons on the cyclohexadienyl moiety (Scheme 3), but we feel that this would not explain the resonances present in the low temperature spectrum satisfactorily. It would also not account for the ready formation of benzene and cyclohexane when a solution of **C** or **D** is warmed to 60°C for a few minutes (see below). The non-reversible insertion of cyclohexene into an $\text{Fe}-\text{H}$ bond to give a cyclohexyl complex has been reported.¹⁶

It remains to assign the stereochemistries of **B** and **C**, for which the four possibilities are shown in Fig. 2, I–IV. Since in **C** the reversible insertion of alkene into the $\text{M}-\text{H}$ bond is occurring, it is probable that the alkene and hydride are mutually *cis*. This, together with the fact that a single sharp ^{31}P NMR resonance (δ 59.7) is observed at all temperatures, suggests that **C** has structure I. Since **B** is so readily converted to **C** it is probable that here again the alkene and the hydride are mutually *cis* and that **B** has structure II or IV.

The compound **C** may then readily be formed from **B** by insertion of alkene into the $\text{M}-\text{H}$ bond followed by elimination in a different sense to give **C** ((b) in Scheme 1). The formation of these complexes from $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ and cyclohexene is outlined in Schemes 1 and 2. It is interesting to note that complexes analogous to **B** and **C** which contain hydrido, alkene and 1-3- η -allyl ligands are

obtained³ from the reaction of $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ with hex-1-ene.

Implications for the alkene insertion reaction. It is clear from the NMR data presented above that the equilibrium (a) in Scheme 2 is *slow* on the NMR time scale, even at 60°C , while the rate of the insertion reaction (Equilibrium (c)) is *comparable* with the NMR time scale. This then represents the first spectroscopically observable system in which it can be unequivocally stated that the rate determining step in the isomerisation of alkenes using catalysts of this kind is alkene coordination rather than hydrogen transfer from the metal to the alkene. The same conclusion has also been reached for other hydridic Ru^{II} systems on the basis of kinetic studies.¹⁷

In principle it is possible to calculate the relative rates of the coordination and insertion steps from NMR data but, in view of the complexity of the system we can be satisfied with the qualitative result.

Although we are unable to say from our data whether the stereochemistry of addition of the $\text{Ru}-\text{H}$ bond across the double bond of cyclohexene is *cis* or *trans*, the fact that only four of the methylene protons take part in the exchange with the metal hydride indicates that the stereochemistry of this addition must be the same as that of elimination from the cyclohexyl ruthenium species to re-form the hydrido alkene complex.

Catalytic disproportionation of cyclohexene to benzene and cyclohexane. When solutions of $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10})$ (**A**, **B** or **C**) are heated to 60°C in deuteriotoluene they become red and all the peaks in the ^1H NMR spectrum below δ 6 disappear to be replaced by sharp resonances attributable to benzene and cyclohexane (GLC evidence shows that benzene and cyclohexane are formed in an approximately 1:1 ratio).

The most rational explanation of this observation is that transfer of hydrogen from the methylene group of the cyclohexadienyl moiety to the transient cyclohexyl group (formed by the insertion of cyclohexene into the $\text{Ru}-\text{H}$ bond of **C**) occurs. This provides direct evidence for the type of mechanism that we have postulated for the removal of hydrogen from the *ortho* position of triphenylphosphine, propene, but-1-ene, pent-1-ene, and cyclooctadiene in related ruthenium systems.^{2,3} We think it unlikely that the hydrogen transfer occurs *via* the metal, but transfer to the metal evidently can occur since heating $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ in the

Scheme 4. Catalytic cycle for the conversion of cyclohexene to benzene and cyclohexane.

presence of PPh_3 causes quantitative conversion to $\text{RuH}_2(\text{PPh}_3)_4$.

The disproportionation of benzene to cyclohexene is evidently catalytic since if 0.2 g $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ is refluxed in cyclohexene (5 ml) for 16 h, GLC data show that 9.8 % of cyclohexane and 4.5 % of benzene are formed. After a further 20 h, 23.7 % cyclohexane and 10 % benzene are present, which represents about 25 catalytic cycles. Note that although in the decomposition of **C** equimolar amounts of benzene and cyclohexane are formed, in the catalytic reaction *two* mol of cyclohexane must be formed per mol of benzene.

The catalytic reaction is slowly poisoned as a black solid, assumed to be ruthenium metal, slowly precipitates. However, at room temperature the reaction will proceed without decomposition to black solid, albeit much more slowly. NMR evidence suggests that $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2$ and $\text{RuH}(\text{C}_6\text{H}_7)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10})$ (**C**) are present at all times in the solution. The proposed mechanism of this reaction is outlined in Scheme 4.

The catalytic disproportionation of cyclohexene to benzene and cyclohexane does not appear to have been previously observed in homogeneous systems but it is known to occur heterogeneously¹⁸ and the related catalytic disproportionation of ethylene to ethane and butadiene has been reported,¹⁹ using a titanium catalyst. Polyhydride complexes of iridium catalyse²⁰ the disproportionation of terminal alkenes with chain length greater than C_4 to alkane and diene.

EXPERIMENTAL

Microanalyses by Butterworth Microanalytical Consultancy Limited, Pascher, Bonn and Imperial College Microanalytical Laboratories. Nuclear magnetic resonance spectra were obtained using Perkin-Elmer R12 (60 MHz) and Varian XL-100-12 (^{31}P) spectrometers, the latter operating in the Fourier transform mode with noise proton decoupling. Narrow band decoupling studies were carried out on a Jeol FX60 60 MHz spectrometer. Infrared spectra were measured on a Perkin-Elmer 457. GLC analyses were carried out on Perkin-Elmer F33 chromatograph with Infotronics integrator attachment using a 4 m column packed with 20 % AgNO_3 - ethyleneglycol on a Chromosorb P support. Melting points were determined in closed capillaries under argon on an Electrothermal melting point apparatus and are uncorrected.

All solvents were thoroughly dried and degassed before use and cyclohexene was purified by shaking with acidified iron(II) ammonium sulfate, washed with water and dried by passing down an alumina column. Cyclohexa-1,3-diene was used from a new bottle without further purification but was stored under nitrogen. The petroleum used has boiling range 40–60 °C.

All operations were carried out under dry oxygen free argon using standard suba-seal and catheter tubing techniques.

1. *Hydrido(1-5-η-cyclohexadienyl)bis(triphenylphosphine)ruthenium(II), cyclohexene (1/1) (A)*. $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ (0.15 g) was stirred with petroleum (5 ml) containing cyclohexene (1.5 ml) at room temperature for 90 min. The resulting yellow solution was filtered and after standing for 3 h the walls of the flask were scratched to induce crystallisation. The pale yellow crystals so formed were collected, washed with petroleum (1 ml) and dried *in vacuo*. On standing, more of the complex crystallised from the mother liquors. Total yield ca. 70 %. This compound was also obtained on recrystallisation of **A**, **B** or **C** from cyclohexene or on crystallisation of **B** or **C** from toluene–petroleum. M.p. 109(d) °C; Anal. $\text{RuP}_2\text{C}_{48}\text{H}_{48}$: C, H, P. ^1H and ^{31}P NMR, see text.

IR (Nujol mull, CsI plates) 3130vw, 3040ms, 3000vw, 2790m, 2760m, 2010m, 1580m, 1570w, 1430s, 1305w, 1295w, 1180m, 1175w, 1150w, 1080ms, 1040w, 1025w, 995w, 960w, 930w, 900w, 870vw, 850w, 830w, 790w, 745s, 735s, 720w, 690s, 650m, 615w, 590m, 530s, 515s, 505s, 490s, 455m, 425m, 420m.

2. *Hydrido(1-3-η-cyclohexadienyl)cyclohexenebis(triphenylphosphine)ruthenium(II) (B)*. $\text{Ru}(\text{C}_8\text{H}_8)_2(\text{PPh}_3)_2$ (0.5 g) was stirred in petroleum (10 ml) containing cyclohexene (3 ml) at room temperature for 16 h. The resulting yellow solid was

collected, washed with petroleum (5 ml) and dried *in vacuo*. Yield ca 80 %. M.p. 115(d) °C; Anal. $\text{RuP}_2\text{C}_{48}\text{H}_{48}$: C, H, P. ^1H and ^{31}P NMR, see text.

IR 3130vw, 3035m, 3002m, 2760s, 1960mbr, 1580w, 1568w, 1480s, 1472s, 1432s, 1427s, 1309w, 1298m, 1260w, 1180m, 1178wsh, 1152w, 1145vw, 1132vw, 1118vw, 1085s, 1068w, 1042w, 1027w, 999w, 992vwsh, 962vw, 955vw, 931w, 914w, 901m, 875w, 860vw, 849w, 835m, 821w, 790m, 749s, 742ssh, 739s, 736ssh, 720m, 705ssh, 698vssh, 692vs, 682ssh, 648m, 618w, 600m, 581w, 538vs, 522vs, 511vs, 499s, 480s, 470wsh, 460m, 432s, 425msh.

3. *Hydrido(1-3-η-cyclohexadienyl)cyclohexene-bis(triphenylphosphine)ruthenium(II)* (**C**). $\text{Ru}(\text{C}_6\text{H}_8)_2(\text{PPh}_3)_2$ was stirred in cyclohexene (2.5 ml) for 2 h whereupon the yellow solution so formed began to precipitate the complex as pale yellow microcrystals. After stirring for a further 1 h, the precipitate was collected, washed with petroleum (2 ml) and dried *in vacuo*. Yield ca 60 %, m.p. 85–90(d) °C. Anal. Found: C 72.6; H 6.1; P 7.8. Calc. for $\text{RuP}_2\text{C}_{48}\text{H}_{48}$: C 73.2; H 6.1; P 7.9. ^1H and ^{31}P NMR, see text.

IR 3072msh, 3050m, 3010m, 2770m, 2040mbr, 1582w, 1570w, 1475s, 1432ssh, 1430s, 1308w, 1299w, 1262w, 1182m, 1158w, 1145w, 1138w, 1082m, 1069w, 1045w, 1026w, 999w, 990vw, 969w, 931w, 919w, 902w, 876w, 855vw, 849vw, 836w, 820vw, 789w, 752s, 739s, 721m, 702vssh, 698vs, 690vs, 682ssh, 650m, 643wsh, 620w, 537vs, 521vs, 510vs, 492vs, 458m, 431m, 425msh, 418msh.

4. *Hydrido(1-5-η-cyclohexadienyl)bis(triphenylphosphine)ruthenium(II)*. (**D**) (a) $\text{RuH}_2(\text{PPh}_3)_4$ (0.18 g) was warmed to 100 °C in toluene (5 ml) containing cyclohexa-1,3-diene (0.5 ml) for 3 min. After cooling at room temperature the resulting pale yellow solution was treated with petroleum (35 ml) and cooled to –20 °C. The yellow crystals that separated over 2 days were collected and dried *in vacuo*. The mother liquors were evaporated to dryness and dissolved with warming in a mixture of toluene (0.5 ml), cyclohexa-1,3-diene (0.5 ml) and petroleum (25 ml). On cooling to –20 °C a further crop of the compound was obtained as yellow microcrystals. Total yield ca. 60 %. When cyclohexene was omitted from this last procedure, the compound dissolved but a copious yellow precipitate of $\text{RuH}_2(\text{PPh}_3)_4$ was rapidly obtained.

(b) $\text{RuH}(1-3-η-\text{C}_6\text{H}_7)(\text{PPh}_3)_2(\text{C}_6\text{H}_{10})$ (**B**) (0.1 g) was dissolved in toluene (5 ml) and the solution evaporated to dryness in a slow stream of nitrogen. On the basis of its infrared spectrum the pale yellow solid was identified as **D** but was not further purified. Yield, ca. 95 %, m.p. 90–95 (d) °C. Anal. $\text{RuP}_2\text{C}_{42}\text{H}_{38}$: C, H, P. ^1H and ^{31}P NMR spectra, see text.

IR 3060msh, 3020m, 3006w, 2780m, 1945mbr, 1580w, 1568w, 1432s, 1429s, 1310w, 1299m, 1203 m, 1174m, 1153w, 1127m, 1088s, 1082ssh, 1068m,

1040w, 1024m, 998w, 965vw, 955vw, 931vw, 919vw, 899w, 881vw, 866vw, 845vw, 832vw, 821w, 775w, 751s, 741s, 737ssh, 721m, 708msh, 699vssh, 695vs, 682msh, 650w, 618w, 599w, 571vw, 537ssh, 535vs, 522vs, 510vs, 495vs, 485msh, 469w, 460w, 438w, 432w, 420m.

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